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NONAQUEOUS ELECTROLYTE

REFERENCE TO RELATED APPLICATIONS

5   This application claims priority to US Provisional application No. 60/437,321, filed
December 31, 2002, and hereby incorporated by reference.

FIELD OF INVENTION

The present invention relates generally to non-aqueous electrolytes, and, more
specifically, to non-aqueous electrolytes for use in supercapacitors.

BACKGROUND OF INVENTION

10   Significant effort has been invested over the years in improving the energy and power of
electrical energy storage devices such as capacitors and batteries. Of particular interest herein
are supercapacitors. These energy storage devices are particularly useful in short term, high-
energy applications such as powering electric vehicles or cellular communication. A typical
supercapacitor comprises carbon-based electrodes and an electrolyte having charged ions which
15   can be ordered about the electrodes to create a potential between the electrodes. Therefore,
critical to the overall performance of a supercapacitor is its electrolyte.

An electrolyte typically comprises an ionic salt dissolved in a solvent. A wide variety of
solvents and salts are available for such use, offering specific advantages depending on the
application being considered (e.g., low temperature vs. high temperature). Generally, non-
20   aqueous electrolytes are preferred from the standpoint of electrochemical stability and are
considered herein in detail. A common non-aqueous electrolyte comprises a salt, e.g., tetraethyl
ammonium tetrafluoroborate (TEABF4), dissolved in an organic solvent, e.g., acetonitrile (AN),
propylene carbonate (PC) or gamma butyrolactone (GBL). Generally, the conductivity of the
electrolyte depends upon its concentration of salt. Unfortunately, the conductivity of non-
25   aqueous electrolytes tends to be limited by the solubility of the salt in the solvent.

A new non-aqueous electrolyte system disclosed in US Patent No. 5,965,054 purportedly
addresses this problem by identifying a class of salts which are highly soluble in non-aqueous
solvents to provide good conductivity. More specifically, the '054 patent discloses a salt

1

consisting of a cation selected from a number of an alkyl substituted, cyclic delocalized aromatics and their perfluoro derivatives, and a polyatomic perfluorinated anion. Among a number of alkyl substituted, cyclic delocalized aromatics disclosed, the '054 patent states that imidazolium, particularly, 1-ethyl-3 methyl imidazolium (EMI) and 1-methyl-3 methyl

5   imidazolium (MMI) in combination with PF6 are preferred because they are particularly soluble and thus can be added in relatively high concentration to a non-aqueous solvent. It is claimed that this high concentration of salt in the non-aqueous solvent correlates to high conductivity.

Although the above-mentioned electrolytes have desirable electrochemical properties that make them suitable for electrolytes, they are, unfortunately, expensive. Therefore, there is a need

10   for a less expensive non-aqueous electrolyte having performance which is at least as good as known electrolytes. The present invention fulfills this need among others.

SUMMARY OF INVENTION

The present invention provides for a relatively inexpensive non-aqueous pyridinium-based electrolyte having electrochemical performance comparable or better than conventional

15   electrolyte systems, even at relatively low concentrations. Specifically, it has been discovered that a salt consisting of a cation of pyridinium (PyH) and an anion of a fluorinated non-metal, such as tetrafluoroborate (BF4$^-$), can be dissolved in certain known solvents such as, propylene carbonate (PC), acetonitrile (AN), and gamma butyrolactone (GBL), to yield an electrolyte having an unexpectedly wide window of electrochemical stability and unexpectedly high

20   conductivity, even at relatively low concentrations.

Although the use of pyridinium as a cation has been disclosed among a host of other alkyl substituted, cyclic delocalized aromatics in US Patent No. 5,965,054, it was never considered individually and its excellent electrochemical performance at relatively low concentrations and its lower cost as compared to the other disclosed alkyl substituted, cyclic delocalized aromatics

25   were not recognized. *To the contrary*, the '054 patent exalts the use of the more expensive 1-ethyl-3 methyl imidazolium (EMI) and 1-methyl-3 methyl imidazolium (MMI) cations over pyridinium primarily due to their high solubility. That is, the '054 patent states that EMI and MMI are particularly soluble and thus can be used in higher concentrations in electrolytes, i.e.,

2

over 2M and even greater than 3M. Since they can be used in higher concentrations, the '054 patent purports that they impart greater conductivity to the electrolyte.

The applicants have discovered, however, that pyridinium has excellent electrochemical properties even at relatively low concentrations. Specifically, the pyridinium cation and a

5   fluorinated anion, such as BF_4-, form a salt which has unexpectedly good conductivity and electrochemical stability at concentrations below 2M. Therefore, the present invention provides for an effective electrolyte salt which is not only relatively inexpensive, but which can also be used in relatively low concentrations. Since less of the inexpensive pyridinium-based salt can be used with satisfactory results, there is a two-fold savings realized by its use. This is a significant

10   and unexpected advantage over conventional and newly introduced non-aqueous salts.

Accordingly, one aspect of the present invention is an electrolyte comprising a pyridinium-based salt at a relatively low concentration. In a preferred embodiment, the electrolyte comprises a salt of pyridinium and a fluorinated anion at a concentration of less than about 2M in a non-aqueous solvent. Preferably, the solvent is an organic solvent, such as a linear

15   ether, cyclic ether, ester, carbonate, formate, lactone, nitrile, dinitrile, amide, sulfone or sulfolane, and, more preferably, an alkyl carbonate, alkyl nitrile or alkyl lactone. In a particularly preferred embodiment, the solvent is propylene carbonate (PC), acetonitrile (AN), or gamma butyrolactone (GBL).

The non-aqueous electrolytes of the present invention may be used in any traditional

20   device or apparatus using an electrolyte. Of particular interest herein is their use in electrical energy storage devices, especially electrochemical capacitors/supercapacitors. The electrolytes can also be used in potentiometric and voltametric electrochemical sensors, photovoltaic devices, fuel cells, and in primary and secondary batteries employing alkali and alkaline earth anode materials so long as the electrolyte contains the cation of the alkali or alkaline earth anode

25   material. Further, the electrolytes of the invention may be used as media for catalysis or electro catalysis.

Accordingly, another aspect of the present invention is a device containing a pyridinium-based electrolyte. In a preferred embodiment, the device is an energy storage device, and, more

3

preferably, a supercapacitor having carbon-based electrode and an electrolyte comprising a
pyridinium-based salt at a concentration of less than about 2M in a non-aqueous solvent.

BRIEF DESCRIPTION OF DRAWINGS

Other features and advantages of the invention will be apparent from the following

5   detailed description of the invention, taken in conjunction with the accompanying drawings in
which:

Figs. 1-3 show the electrochemical stability for various concentrations of PyHBF4 in PC;

Figs. 4-7 show the electrochemical stability for various concentrations of PyHBF4 in AN; and

Figs. 8 & 9 show the electrochemical stability for various concentrations of PyHBF4 in GBL.

10   ## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The non-aqueous electrolytes of the invention are superior to conventional electrolytes in
a number of respects that serve to make them particularly useful in electrical energy storage
devices. Specifically, we have determined that pyridinium (PyH^+) based salts can be dissolved
in an organic solvent to provide an electrolyte having excellent electrochemical properties. Such

15   electrolytes can be used in a host of electrochemical applications and are particularly useful in
carbon-based electrode supercapacitors.

The salt of the present invention comprises the cation pyridinium and an anion. The ions
are selected to complement one another such that when the ionic compound is dissolved in an
organic solvent, the ions readily dissociate and have good mobility in the organic solvent to align

20   with their respective electrodes. To this end, the ions are small enough to promote mobility
through the solvent, but are not so small as to be solvated excessively to become, in effect, larger
compounds with compromised mobility. With these criteria in mind, the cation pyridinium in
combination with a perfluorinated non-metal anion is preferred. Preferred non-metal ions
include boron, phosphorous, sulfur, arsenic and antimony. Alternatively, the anion may be

25   selected from the group consisting of perfluoroalkylborates, perfluoroalkylphosphates,
perfluoroalkylsulfonates ($C_nF_{2n+1}SO_3^-$, with n=0, 1, 4, 6, 8), perfluoroalkyl-substituted imides, in
particular bis(trifluoromethylsulfonyl) imide (prepared, for example, in accordance with U.S.
Patent No. 45,054,997), and perfluoroalkyl-substituted methanides, in particular

4

tris(trifluoromethylsulfonyl)methanide (prepared, for example, in accordance with U.S. Patent
No. 5,273,840). More preferably, the anion comprises tetrafluoroborate (BF4-).

5   The cation pyridinium in combination with the anion tetrafluoroborate was found to have
unexpectedly good ionic properties including excellent mobility, conductivity and
electrochemical stability. Furthermore, given the relatively low cost of pyridinium, the PyHBF4
salt is substantially less expensive than traditional salts such as tetraethyl ammonium
tetrafluoroborate and EMIPF6.

10   Pyridinium tetrafluoroborate is a known material and can be prepared very economically
using known techniques. For example, it can be prepared using the procedures and techniques
disclosed in (Polyhedron Vol. 4,pp 787-789 (1985). The pyridinium tetrafluoroborate should be
relatively pure, preferably high purity grade with low water and oxygen content (<30 ppm). It is
important that water and oxygen impurities be minimized as they have a particularly detrimental
15   effect on the electrochemical performance of the salt.

Although PyHBF4 is the preferred salt in the electrolyte of the present invention, it may
be preferable to augment the electrolyte with a conventional conductive salt, e.g.,
tetraalkylammonium or tetraalkylphosphonium salt, to customize it for a particular application.
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Since an electrolyte is a system of ions in a solvent, the solvent is important and affects
directly the performance of the electrolyte. Preferably, the non-aqueous solvent is an organic
solvent. More preferably, the organic solvent is a linear ether, cyclic ether, ester, carbonate,
formate, lactone, nitrile, dinitrile, amide, sulfone or sulfolane, and, even more preferably, is an
25   alkyl carbonate, alkyl nitrile or alkyl lactone. In a particularly preferred embodiment, the solvent
is propylene carbonate (PC), acetonitrile (AN), or gamma butyrolactone (GBL).

It may be preferable to use a combination of PC, AN and GBL for a particular
application. Likewise, it may be preferable to use a combination of two or more non-aqueous
30   solvents mentioned in the paragraph above for a particular application.

Suitable electrolytes must have high conductivity and good electrochemical stability. The power output capability of an energy storage device depends on the working voltage and the maximum current output capability of the electrolyte in combination with the electrodes. The

5   working voltage is directly related to the electrolyte's electrochemical stability while the maximum current output (at least in the double layer type supercapacitors) is mainly dictated by the electrolyte's conductivity.

To evaluate an electrolyte's electrochemical stability, the electrolyte is subjected to cyclic

10   voltammetry to determine its "voltage window." As used herein, the term "voltage window" refers to the voltage range which the electrolyte can tolerate without substantially reacting (i.e., undergoing reduction or oxidation). To determine the voltage window, an electrolyte is placed in a cell having a working electrode, a counter electrode, and a test electrode, which is immediately adjacent but not touching the working electrode. The electrodes in the cell are connected to a

15   cyclic voltammetry apparatus, called a potentiostat, which is configured to adjust the current between the working and counter electrodes to maintain a "desired voltage" between the working electrode and the reference electrode. The voltage between the reference electrode and the working electrode can be varied as a function of time in a programmed manner (for example, suitable results have been obtained using a linear change rate of 20 mV/s). The voltage window

20   is determined by progressively increasing the desired voltage (in both the positive and negative directions) until there is a precipitous increase in the current required to drive the working and counter electrodes to maintain the desired voltage. The sharp rise in current at the end voltages generally indicates the breakdown voltage of the electrolyte, meaning that the salt or the solvent is undergoing a reduction reaction at the negative end voltage or an oxidation reaction at the

25   positive end voltage. Such reactions could include gas evolution or simple oxidation/reduction reactions. The voltage difference between these two end voltages at which the current reaches a predetermined value, for example 100 mA/cm2, is called the electrochemical window or "voltage window."

6

The voltage window of pyridinium-based electrolytes is considerably higher than one would expect. For example, an electrolyte of PyHBF4 in PC at a concentration of 1.02M has a voltage window of 4 volts, an electrolyte of PyHBF4 in AN at a concentration of 0.59 M solution has a voltage window of 3.5 V, and an electrolyte of PyHBF4 in GBL at a concentration of
5   1.62M solution has a voltage window of 4 volts. The voltage window of 4 V for PyHBF4 in PC and GBL is higher than that of conventional electrolyte systems and provides high power capability for supercapacitor applications. Furthermore, the voltage window for all three solvents is generally constant for different pyridinium concentrations. Such constant stability across a range of salt concentrations is advantageous. Accordingly, the electrolyte of the present
10   invention has a voltage window preferably of at least 3.5 V and, more preferably, of at least 3.8 V.

The conductivity for pyridinium-based electrolytes is comparable to prior art electrolyte systems, and is particularly good for PyHBF4 in AN and GBL, even at low concentrations. For example, an electrolyte of PyHBF4 in PC at a concentration of 1.02M solution has a conductivity
15   of 10.53 mS/cm, an electrolyte of PyHBF4 in AN at a concentration of 0.59 M solution has a conductivity of 32 mS/cm, and an electrolyte of PyHBF4 in GBL at a concentration of 1.62m/l has a conductivity of 20.2 mS/cm. By way of comparison, EMIPF6/PC has a maximum conductivity of 15.3 mS/cm at 2M concentration ('054 patent, Table 2), and the maximum conductivity for 1M TEABF4/PC is 13 mS/cm (Ue et al., J. Electrochem. Soc. 141:2989, 1994).
20   The conductivities of the pyridinium-based electrolytes compare favorably with these electrolyte systems, and, the PyHBF4/AN and PyHBF4/GBL systems, in particular, compare favorably with these maximum conductivities of conventional electrolytes, even at lower concentrations.

The concentration of the PyHBF4 in the solvent can be tailored to the application's particular needs. The preferred concentration of the electrolyte for the supercapacitor application
25   is one at which the conductivity and the electrochemical window are maximum. Since the voltage window is generally constant for the various concentrations, optimization will typically be a function of optimizing conductivity. Furthermore, since the high surface area activated carbon electrodes are standard for non-aqueous systems, the power output capability depends mainly on the electrolyte conductivity. Higher electrolyte conductivity leads to lower internal
30   voltage drop in the capacitor. Generally, increasing the concentration of the salt in the solvent

7

will improve the electrolyte's conductivity which, in turn, improves its performance as an

electrolyte. Accordingly, if the objective is to maximize conductivity, it is preferable to saturate

the electrolyte composition with salt. However, if a particular conductivity can be met using a

lower concentration of salt, cost considerations would dictate using sub-saturation levels of salt.

5   Generally, it is preferred that the concentration of pyridinium-based salt be less than 2M. More

preferably, the concentration is less than 1.75M and, still more preferably, around 1.0M. With

respect to PC, it has been found that suitable results have been obtained with a concentration of

PyHBF4 below 1.02 M. With respect to AN, suitable results have been obtained with a

concentration of PyHBF4 of less than 1.1M. With respect to GBL, suitable results have been

10   obtained with a concentration of PyHBF4 less than about 1.62 M.

The excellent electrochemical performance and the relatively low cost of pyridinium-

based electrolytes make them ideal for use in electrolyte systems in batteries and capacitors,

including single cell and multi-cell capacitor devices, and other non-aqueous electrochemical

capacitors, such as the Type III redox polymer system (Ren et al. Electrochemical Capacitors,

15   F.M. Delnick and M. Tomkiewicy, Editors, PV95-29, p.15, The Electrochemical Society

Proceedings Services, Pennington, N.J. (1996); Arbizzani et al., Adv. Mater. 8: 331, 1996).

The examples below are provided to illustrate the invention and should not be construed

as limiting the invention to the particular embodiments disclosed therein.

Example 1

20   Solutions of varying concentrations of PyHBF4 in PC were prepared by mixing high

purity propylene carbonate solvent (Honeywell's high purity PC used in Digirena® electrolyte)

and high purity PyHBF4 (Sigma Aldrich Co.). The PyHBF4 was transferred from its sealed

original container to a glove box. The moisture level and the oxygen level in the glove box was

maintained below 1 and 2 ppm, respectively. Such limitations are preferred, however, moisture

25   and oxygen levels below 10 ppm may be adequate. In preparing a saturated electrolyte solution,

a known quantity of the high purity propylene carbonate solvent was transferred to a glass

container with a cap or lid. A known amount of pyridinium tetrafluoroborate was added to the

container and mixed until all of the added quantity of the solid salt was dissolved. To facilitate

dissolution, a magnetic stirrer bar is placed inside the solution and stirred well by placing it on a

8

magnetic stirrer. After the salt is dissolved, another small known quantity of the salt was added and the procedure was repeated until trace amounts of undissolved salt were visible. The amount of the salt and the solvent were used to calculate the solubility of the salt in propylene carbonate. This is the highest concentration solution indicated in Table 1. Solutions of varying

5   concentrations other than saturated were prepared by dissolving the required amount of the salt in the required amount of the solvent. It can also be prepared by diluting the saturated solution with the required amount of the solvent. These less-than-saturated solutions are also listed on Table 1.

Each concentration above was subjected to cyclic voltametry to determine its voltage

10   window. The voltage window was determined using an electrochemical microcell. The microcell comprised electrodes mounted to its top. Specifically, a 3mm diameter polished glassy carbon rod was used as a working electrode. This rod was covered on the cylindrical surface with a plastic sheath. A silver wire was used as a reference electrode. The tip of the silver wire is placed as close to the working electrode as possible without touching it (i.e., approximately

15   1mm). A platinum foil was used as a counter electrode. The electrodes are connected to an EG&G Princeton Applied Research Corp M273A Potentiostat. The operation of the potentiostat was controlled by a desktop/personal computer using PARC M270 Research Electrochemical software.

In determining the voltage window for each concentration, approximately 15 ml of

20   solution of each concentration was transferred to the microcell described above and an initial voltage was measured. This is known as rest potential or open circuit potential. The current was substantially zero at this time. Then the voltage between the working electrode and the reference electrode is continuously cycled between a positive voltage limit and a negative voltage limit by changing the voltage at a constant rate. The voltage changes from the rest potential to one

25   voltage limit, then to the other voltage limit and finally ending at the rest potential where it started. The current that flows between the working electrode and the counter electrode in response to the above voltage change was measured. The voltage-current data is plotted in graphical form and is called a cyclic voltammogram.

The graph produced by this technique for the PyHBF4/PC electrolyte solution is

30   presented in Figs. 1 - 3 for various concentrations up to the saturation limit of 1.02 M.

9

Generally, the presence of a current peak on the top half or the bottom half of the graph indicates respectively an electrochemical reduction or oxidation process taking place at the potential corresponding to the peak location. In this electrolyte and electrode system there is no oxidation or reduction peak. It means that this electrolyte is stable through the voltage window indicated

5   by the sharp rise in the current level at the end voltages. In this case we see an electrochemical window of nearly 4 V. This is comparable to or higher than any known state of the art electrolyte system.

The conductivity of each solution was measured using a VWR NIST-Traceable conductivity meter. The conductivity as a function of the electrolyte concentration is shown in

10   Table 1.

Table 1

Initial rest potential of the PyHBF4/PC electrolyte solutions and their conductivity

Concentration (M)	Rest Potential (V)	Conductivity (mS/cm)	Voltage Window (V)
0.25	0.277	4.5	4.00
0.38	0.317	5.9	4.00
0.51	0.278	7.2	4.00
0.75	0.424	9.1	4.00
1.02	0.563	10.5	3.90

20   Thus, the figures and the table provide evidence to the electrochemical performance of this electrolyte at different concentrations. Even at relatively low concentrations, for example, below 1M, the electrochemical performance of the pyridinium-based salt is relatively good compared to prior art. Generally, the preferred concentration of the electrolyte for the supercapacitor application is one at which the conductivity and the electrochemical voltage

25   window are maximum. Since the voltage window remains fairly constant at all concentrations, selecting a preferred concentration becomes a function of desired conductivity. Higher concentrations equate to higher conductivities.

Example 2

Solutions of varying concentrations of PyHBF4 in acetonitrile were prepared by mixing high purity acetonitrile solvent (Honeywell's high purity acetonitrile used in Digirena® electrolyte) and high purity PyHBF4 (supplied by Sigma Aldrich Co,) in the same way was discussed above with respect to Example 1.

The voltage window was determined using the same apparatus and procedure as described above with respect to Example 1. The graph produced by this technique is presented in Figures 4-7 for the concentrations 0.33 m/l and 0.22 m/l of pyridinium tetrafluoroborate in acetonitrile. Generally there will be current peaks on the top half or the bottom half of the graph if there are electrochemical reduction or oxidation processes occurring at any potential in this voltage window. In the PyHBF4/AN case there are no such electrochemical reactions observed other than at the end voltages. In this case we see an electrochemical window of 3.5 V as shown in Table 2. This is comparable to or higher than the state of the art electrolyte, tetraethyl ammonium tetrafluoroborate/acetonitrile (TEABF4/AN).

The conductivity of each solution was measured in the same manner as described in Example 1. The conductivity as a function of the electrolyte concentration is shown in Table 2. Thus, the figures and the table provide evidence to this capability of the herein disclosed new electrolyte.

Table 2

Initial rest potential of the PyHBF4/AN electrolyte solutions and their conductivity

Concentration (M)	Rest Potential (V)	Conductivity (mS/cm)	Voltage Window (V)
0.22	0.42	7.27	3.55
0.33	0.394	22.5	3.85
0.46	0.383	28.2	3.85
0.59	0.264	31.9	3.75
0.75	0.330	35.1	3.85
1.00	0.275	41.04	3.90
1.14	0.245	51.56	3.90

Thus, the figures and the table provide evidence to the electrochemical performance of this electrolyte at different concentrations. Even at relatively low concentrations, for example,

11

below 1M, the electrochemical performance of the pyridinium-based salt is relatively good compared to prior art. Generally, the preferred concentration of the electrolyte for the supercapacitor application is one at which the conductivity and the electrochemical voltage window are maximum. Since the voltage window remains fairly constant at all concentrations,

5   selecting a preferred concentration becomes a function of desired conductivity. Higher concentrations equate to higher conductivities.

Example 3

Solutions of varying concentrations of PyHBF4 in gamma butyrolactone solvent were prepared by mixing high purity gamma butyrolactone solvent (Honeywell's high purity gamma

10   butyrolactone solvent used in Digirena® electrolyte) and high purity PyHBF4 (supplied by Sigma Aldrich Co,) in the same way was discussed above with respect to Example 1.

The voltage window was determined using the same apparatus and procedure as described above with respect to Example 1. The graph produced by this technique for the PyHBF4/PC electrolyte solution is presented in Figs. 8 & 9 for various concentrations up to the

15   saturation limit of 1.62 m/l. Generally presence of a current peak on the top half or the bottom half of the graph indicates respectively an electrochemical reduction or oxidation process taking place at the potential corresponding to the peak location. In this electrolyte and electrode system there is no oxidation or reduction peak. It means that this electrolyte is stable through the voltage window indicated by the sharp rise in the current level at the end voltages. In this case

20   we see an electrochemical window of nearly 4 V. This is comparable to or higher than any known state of the art electrolyte system.

The conductivity of each solution was measured using a YSI 3200 conductivity meter. The conductivity as a function of the electrolyte concentration is shown in Table 3. Thus, the figures and the table provide evidence to this capability of the herein disclosed new electrolyte.

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Table 3

Initial rest potential of the PyHBF4/GBL electrolyte solutions and their conductivity

Concentration (M)	Rest Potential (V)	Conductivity (mS/cm)	Voltage Window (V)
0.25	0.225	6.6	4.00
0.33	0.085	8.1	4.00
0.55	0.035	11.5	4.00
0.62	0.260	11.8	3.95
0.75	0.125	13.7	4.00
1.00	0.110	14.8	4.00
1.20	0.050	16.2	3.90
1.61	0.101	20.2	3.95

Thus, the figures and the table provide evidence to the electrochemical performance of this electrolyte at different concentrations. Even at relatively low concentrations, for example, below 1M, the electrochemical performance of the pyridinium-based salt is relatively good compared to prior art. Generally, the preferred concentration of the electrolyte for the supercapacitor application is one at which the conductivity and the electrochemical voltage window are maximum. Since the voltage window remains fairly constant at all concentrations, selecting a preferred concentration becomes a function of desired conductivity. Higher concentrations equate to higher conductivities.